Determination accuracy of analysis refractory materials by X-ray fluorescence

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Determination accuracy of analysis refractory materials by X-ray fluorescence

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Abstract. This work was focused on the finding of the right way how to analyze refractory materials by X-ray fluorescence. This method can provide accurate results which can be easily repeated, what is the reason why this method is commonly used in industry. Using of the fluorescent spectrometric analysis comes with one issue, which is the presence of many distorting interferences. From this particular reason it is necessary to identify these interferences and then find the ideal solution for their elimination. The choosing of the right method of sample preparation is basic point for making of well analyze results. The differences are shown on the refractory materials samples. All the values were compared according to standards compositions. In this case we compare different conditions of measurement, under air and vacuum. And different preparation form in powder or fusion into pearl.

1. Introduction

1.1. X-ray spectrometry

In this method, the inner electron is pulled out of its atomic orbit via the absorption of shortwave radiation (photon) with a sufficient amount of energy [1]. The photon energy must be greater than the energy that binds the electron to the core of the atom. If the inner electron is thrown out of the atom, the electron from the higher energy level moves to its place. At this transition, the photon is emitted by the specific energy characteristic of the atom [2]. This fluorescence radiation is called a characteristic X-ray radiation, the energy of the radiated photon being equal to the energy difference of the orbital represented by the transition of the electrons [3].

1.1.1. Energy disperse x-ray spectrometry (EDXRF). EDXRF is one of two main types of X-ray fluorescence techniques used for elemental sample analysis. With EDXRF spectrometers, all elements in the sample are excited simultaneously and energy dispersive detector combined with multiple channel analyzer together, collects the fluorescence radiation emitted from the sample. Then analyzer divides it on the basis of the different energy of the characteristic radiation of the various elements present in the sample. Resolution of EDXRF spectrometer depends on the radiation detector (typically in the range 150–600 eV). The benefits of this system are its simplicity, fast operation, the absence of moving fine parts and high efficiency [6]. It requires x-ray source, which is found in most laboratory instrument with a power of 50–60 kV tube. Next crucial component is X-ray detector, which is designed to convert the intensity of energy levels detected into electrical pulses [7]. In addition to the source and the X-ray detector, its filters, targets and collimators are also important. These types of

filters are found in almost all EDXRF devices. Their function is to absorb or, on the contrary, excite and transfer the energy of some X-ray sources more than other. These filters ensure that if we are interested in measuring a certain type of atoms on an EDXRF device, by using the filter, we will prefer to measure these interest elements and to suppress the measured values of similar properties as the interest element, thus avoiding the partial merging of these values [8]. Energy disperse spectrometry device is schematically shown at Figure 1.

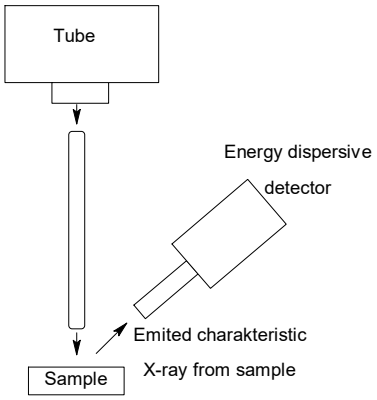

Figure 1. EDXRF device.

2. Experimental part

All samples were measured using the XENEMETRICS EX-6600 SSD energy dispersing device. It is energy dispersive X-ray spectrometer which has secondary polarizing filters, the primary targets for measurement and specification and secondary collimator. This instrument can also measure without standardized methods. It is able to determine the qualitative and quantitative composition of elements in the sample from fluoride to uranium. However, to improve the accuracy of measurement, it is necessary to calibrate the device for specific material [4]. For the measurement, was sample modified into two forms, powdered and fused into a pearl. For comparison, the samples were measured under various conditions in the presence of air or vacuum. The evaluation of measurements was carried out using the Fundamental Parameters software and through calibration using purchased standards of refractory materials The Okayama Ceramics Research Foundation [5].

2.1. Sample preparation

For determination of refractory materials has been chosen two different forms of sample. It was the form as powder and fusion into borate pearls.

2.1.1. Powder measurement. Measured material was first milled on a mill and then filled into capsules for measurement on an XRF spectrometer. These capsules are on the side adjacent to the radiation source and the detector covered with the radiation permeable film.

2.1.2. Measurement in the form of fused pearls. The advantage of measuring in the form of pearls against the measurement of powder samples is to suppress the matrix effect and thus to obtain more accurate results. It is important to choose right mix of flux that will be used. For this reason, so-called acidity indexes are used to tell us what proportion of the flux to use.

2.2. Device parameters for individual measurement

For analysis, it was important, among other things, to find suitable measurement parameters for each sample form (powder / pearl) and the environment in which the measurements were to take place (air / vacuum). The main set parameters are the time of measurement and setting of the X-ray lamp. For

the X-ray lamp, the amount of supply voltage and current is set. The voltage value has been set to 20 kV. The largest energy required for excitation is iron (6.4 kV). Normally, it is recommended to multiply the maximum value of element excitation by 1.6 times during measurements, but the 20 kV setting is recommended based on experimental experience [9]. The measurement settings are shown in Table 1.

Table 1. Table values of electric current and voltage.

Sample	Voltage [kV]	Eletric current [μA]
Powder in air	20	1900
Powder in vacuum	20	1200
Pearl in air	20	1100
Pearl in vacuum	20	1100

2.3. Calculation of acidity index of individual standards

For calibration, the standards of The Okayama Ceramics Research Foundation were used [10]. This set of standards contains ten samples of refractory materials with different percentage composition of oxides. The theoretical acidity index for each sample were calculated as shown in the Table 2, on the basis of which the average acidity index was then displayed in the table on which the melt blend was assembled. The resulting composition of a suitable melting mixture has to be verified and optimized based on experiments.

Example of acidity index calculation for standard JRRM 301:

Silica SiO2:

$$\text{Acidity index} = \frac{\text{Number of oxygen atoms}}{\text{Number of other atoms}} = \frac{2}{1} = 2 \tag{1}$$

Calculation of the contribution to the acidity index of the sample by silicon dioxide

$$\text{SiO}_2 \text{ in JRRM 301} = \frac{x\,[\%]}{100\,[\%]} \cdot \text{Ai}_{(\text{SiO}_2)} = \frac{43.9}{100} \cdot 2 = 0.88 \tag{2}$$

Calculation of theoretical sample acidity index

$$\text{JRRM 301} = \sum \text{Ai}_{(\text{XO}_y)} = 1.69 \tag{3}$$

Table 2. Table of calculated acidity index for sample JRRM 301.

Oxide	Percentage of sample [%]	Oxide acidity index	Theoretical acidity index of the oxide in the sample
SiO_2	43.9	2	0.88
Al_2O_3	46.8	1.5	0.70
Fe_2O_3	3.53	1.5	0.05
TiO_2	1.03	2	0.02
MnO	0.01	1	0.00
CaO	0.79	1	0.01
MgO	0.69	1	0.01
Na_2O	0.17	0.5	0.00
K_2O	2.01	0.5	0.01
B_2O_3 [a]	0.87	1.5	0.01
		Theoretical sample acidity index:	1.69

[a] Uncertified value

Theoretical acid numbers were calculated for all standards and are shown in Table 3. The average value of the acidity index of the refractory material was approximately 1.5. This value suggests that this material will have to be fused using more basic lithium metaborate. However, the metaborate itself undergoes crystallization, which is why the mixture was prepared by mixing lithium metaborate with lithium tetraborate in a 3:1 ratio. The total weight was 5 g of flux and 0.5 g of the powder sample. The thus prepared weights were placed in a platinum crucible in a fusion machine where the sample fused and the melt was then poured onto the platinum dish in which the pearl was cooled.

Table 3. Table with calculated acidity index of standards.

Sample	JRRM 301	JRRM 302	JRRM 303	JRRM 304	JRRM 305	JRRM 306	JRRM 307	JRRM 308	JRRM 309	JRRM 310	**Average acidity index**
Acid number	1.69	1.67	1.66	1.64	1.57	1.56	1.52	1.55	1.51	1.49	**1.59**

3. Results and discussion

3.1. *Measurement of standards by the fundamental parameter method*
Samples were measured and the percent of the individual oxides in the sample was calculated using the Fundamental parameters software. These values vary considerably from the certified standards. By using this method, inaccurate results were obtained, as can be seen in the Figure 2.

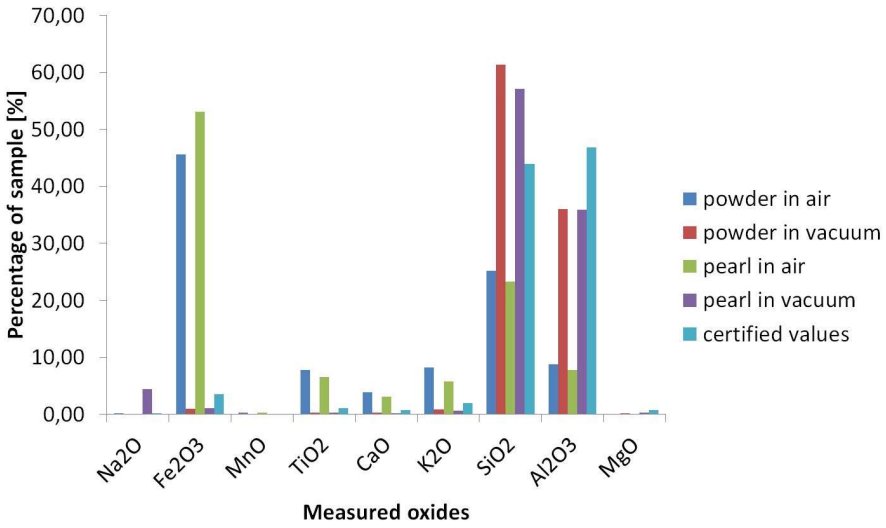

Figure 2. Measured values calculated by fundamental parameters method of JRRM 301 sample.

3.2. Calibration by using standards
Calibration was made on the basis of the measured spectra of a set of standardized samples. In the measured spectrum, the certified values of oxides in the standards were always entered manually. These values were used to construct the calibration curve by linear regression.

Table 4. Sample JRRM 301, powder in air.

Oxides in standard	Percentage of oxides [%]	Calculated percentage of oxide by FP [%]	Relative deviation by FP [%]	Absolute deviation by FP [%]	Calculated deviation after calibration [%]	Relative deviation after calibration [%]	Absolute deviation after calibration [%]
Na_2O	0.17	0.13	22.19	0.04	0.56	228.99	0.39
Fe_2O_3	3.53	45.64	1192.94	42.11	2.41	31.68	1.12
MnO	0.01	0.28	2702.70	0.27	0.00	69.82	0.01
TiO_2	1.03	7.78	655.57	6.75	0.68	33.97	0.35
CaO	0.79	3.91	395.07	3.12	0.55	30.37	0.24
K_2O	2.01	8.23	309.61	6.22	1.54	23.58	0.47
SiO_2	43.90	25.14	42.73	18.76	43.78	0.26	0.12
Al_2O_3	46.80	8.80	81.19	38.00	50.11	7.08	3.31
MgO	0.69	0.08	88.95	0.61	0.36	47.30	0.33

Table 5. Sample JRRM 301, powder in vacuum.

Oxides in standard	Percentage of oxides [%]	Calculated percentage of oxide by FP [%]	Relative deviation by FP [%]	Absolute deviation by FP [%]	Calculated deviation after calibration [%]	Relative deviation after calibration [%]	Absolute deviation after calibration [%]
Na_2O	0.17	0.13	26.45	0.04	0.35	108.77	0.18
Fe_2O_3	3.53	0.97	72.56	2.56	2.31	34.55	1.22
MnO	0.01	0.01	41.01	0.00	0.00	93.45	0.01
TiO_2	1.03	0.33	68.27	0.70	0.69	33.09	0.34
CaO	0.79	0.25	68.90	0.54	0.56	29.42	0.23
K_2O	2.01	0.82	59.33	1.19	1.41	29.62	0.60
SiO_2	43.90	61.33	39.71	17.43	44.29	0.89	0.39
Al_2O_3	46.80	35.97	23.15	10.83	49.87	6.57	3.07
MgO	0.69	0.21	69.40	0.48	0.51	26.00	0.18

Table 6. Sample JRRM 301, pearl in air.

Oxides in standard	Percentage of oxides [%]	Calculated percentage of oxide by FP [%]	Relative deviation by FP [%]	Absolute deviation by FP [%]	Calculated deviation after calibration [%]	Relative deviation after calibration [%]	Absolute deviation after calibration [%]
Na_2O	0.17	0.10	40.60	0.07	0.42	147.05	0.25
Fe_2O_3	3.53	53.14	1405.27	49.61	2.66	24.68	0.87
MnO	0.01	0.28	2694.71	0.27	0.01	24.46	0.00
TiO_2	1.03	6.57	538.20	5.54	0.73	29.19	0.30
CaO	0.79	3.07	289.15	2.28	0.55	30.71	0.24
K_2O	2.01	5.75	185.92	3.74	1.61	19.82	0.40
SiO_2	43.90	23.28	46.98	20.62	46.83	6.69	2.93
Al_2O_3	46.80	7.81	83.31	38.99	46.65	0.31	0.15
MgO	0.69	0.00	99.95	0.69	0.53	22.93	0.16

Table 7. Sample JRRM 301, pearl in vacuum.

Oxides in standard	Percentage of oxides [%]	Calculated percentage of oxide by FP [%]	Relative deviation by FP [%]	Absolute deviation by FP [%]	Calculated deviation after calibration [%]	Relative deviation after calibration [%]	Absolute deviation after calibration [%]
Na_2O	0.17	4.43	2503.34	4.26	0.42	149.16	0.25
Fe_2O_3	3.53	1.11	68.58	2.42	2.93	17.08	0.60
MnO	0.01	0.01	42.95	0.00	0.01	44.68	0.00
TiO_2	1.03	0.29	72.10	0.74	0.82	20.14	0.21
CaO	0.79	0.20	75.18	0.59	0.59	24.78	0.20
K_2O	2.01	0.59	70.43	1.42	1.79	10.90	0.22
SiO_2	43.90	57.15	30.18	13.25	45.25	3.07	1.35
Al_2O_3	46.80	35.92	23.26	10.88	47.79	2.12	0.99
MgO	0.69	0.32	53.93	0.37	0.39	44.15	0.30

4. Conclusion

For powder calibration, the measurement was more accurate than the fundamental parameter method, and in the vacuum the measurement was more accurate than in the air. Highest absolute deviations were up to 6% in air and 3% in vacuum measurements. Parameters for setting the electric current for powder was about 700 mA higher in air than when it was measured in a vacuum. This difference is mainly due to the interaction of the primary radiation of the lamp with the molecules contained in the air.

For calibration in the form of a pearl, the results were further refined compared to those measured in powder form. This refinement is mainly due to the suppression of the matrix effect by dissolving the sample in the melt. As with other methods, it was true that vacuum measurements were more accurate than in the air. Highest absolute deviations were up to 3% in air and 1,5% in vacuum measurements. Parameters for the pearl sample are the same as in the air and in the vacuum. However, this setting is lower by 100 μA than in the form of powder in the vacuum. This is because during measuring in powder form the radiation passes through the cover sheet and also there are different sizes of measured particles.

Acknowledgements

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